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Patentanmeldung Nr. Patent application No. Demande de brevet n°

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(Falls die Bezeichnung der Erfindung nicht angegeben ist, siehe Beschreibung.  
If no title is shown please refer to the description.  
Si aucun titre n'est indiqué se référer à la description.)

Dyes comprising ((4-(2-amino-3,6-disulpho-8-hydroxynaphth-1-ylazo)anilino)-1,3,5-triazinyl) moities

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**Dyes comprising [(4-[2-amino-3,6-disulpho-8-hydroxynaphth-1-ylazo]anilino)-1,3,5-triazinyl] moities**

This invention relates to dyes, to inks and to their use in ink jet printing and classical dyeing operations and classical printing operations.

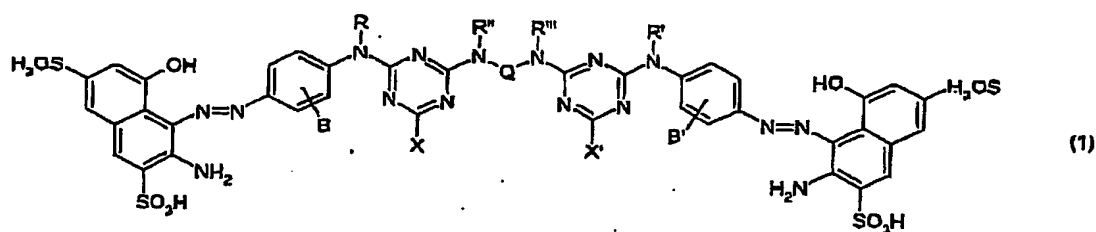
Classical or conventional dyeing operations comprise exhaustion dyeing which works by diffusion of the dissolved dye into the fibers (batch and continuous dyeing).

Classical or conventional printing processes are well known and differ in the way the printing ink or printing paste is transferred to the substrate: For example, inks or pastes can be applied by raised type (e.g. letter press, flexographic), from a planar surface (lithographic), from a recessed surface (intaglio) or through a stencil (silk screen).

Different methods of application and different substrates require different properties in the ink. These operations are described for example in M. Peter, H. K. Rouette: *Grundlagen der Textilveredlung, Handbuch der Technologie, Verfahren, Maschinen*, 13th ed., Deutscher Fachverlag, Frankfurt 1989 (ISBN 3-87150-270-4) in the chapter 7.222.1 and chapter 7.222.2 on the page 484 to the page 495.

Dyes comprising bis[(4-[2-amino-3,6-disulpho-8-hydroxynaphth-1-ylazo]anilino)-1,3,5-triazinyl] moities are known from GB2331757. EP693538 A2 discloses mixtures of non-reactive, bridged monoazo direct dyes carrying triazine groups which are substituted by a piperazino group or a diamino group. However there is still a need for dyestuff haveing bis[(4-[2-amino-3,6-disulpho-8-hydroxynaphth-1-ylazo]anilino)-1,3,5-triazinyl] moities with improved properties, especially improved fastness to light.

According to the present invention there is provided a bis-azo compound of Formula (1) and salts thereof:



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wherein:

B and B' are each independently -SO<sub>3</sub>H, -COOH, ~~-CF<sub>3</sub>~~, substituted alkoxy, substituted alkyl, unsubstituted alkoxy, unsubstituted alkyl, or -PO<sub>3</sub>H<sub>2</sub>;  
Q is an organic aliphatic linking group;  
R, R', R" and R''' are each independently H or unsubstituted or substituted alkyl;  
X and X' are each independently a labile atom or group ;

10 B and B' are preferably attached ortho to the azo group. Preferably B and B' are each independently -SO<sub>3</sub>H, -COOH, alkoxy (preferably substituted C<sub>1-4</sub>-alkoxy or substituted C<sub>1-4</sub>-alkoxy), alkyl (preferably unsubstituted C<sub>1-4</sub>-alkyl or substituted C<sub>1-4</sub>-alkyl) or -PO<sub>3</sub>H<sub>2</sub>, more preferably -SO<sub>3</sub>H or -COOH and especially -SO<sub>3</sub>H. When B or B' are substituted alkyl or substituted alkoxy the substituents are selected from -OH,  
15 -SO<sub>3</sub>H, -COOH, -NH<sub>2</sub>, C<sub>1-4</sub>-hydroxyalkyl, C<sub>1-4</sub>-hydroxyalkoxy and C<sub>1-4</sub>-alkoxy. In preferred compounds B is equal to B'.

Preferably R, R', R" and R''' are each independently H or unsubstituted C<sub>1-4</sub>-alkyl or substituted C<sub>1-4</sub>-alkyl substituted by hydroxy, carboxy, sulpho or cyano or unsubstituted  
20 C<sub>1-4</sub>-alkoxy or substituted C<sub>1-4</sub>-alkoxy substituted by hydroxy, carboxy, sulpho or cyano. More preferably R, R', R" and R''' are each independently H or unsubstituted C<sub>1-4</sub>-alkyl or C<sub>1-4</sub>-alkyl substituted by hydroxy, carboxy, sulpho or cyano. It is especially preferred that R, R', R" and R''' are methyl or H, more especially H.

25 When R, R', R" and R''' are substituted alkyl or substituted alkoxy the substituents are selected from -OH, -SO<sub>3</sub>H, -COOH, -NH<sub>2</sub>, C<sub>1-4</sub>-hydroxyalkyl, C<sub>1-4</sub>-hydroxyalkoxy and C<sub>1-4</sub>-alkoxy.

30 Preferably R''' is H while R" H or unsubstituted C<sub>1-4</sub>-alkyl or substituted C<sub>1-4</sub>-alkyl substituted by hydroxy, carboxy, sulpho or cyano or unsubstituted C<sub>1-4</sub>-alkoxy or substituted C<sub>1-4</sub>-alkoxy substituted by hydroxy, carboxy, sulpho or cyano.

The organic aliphatic linking group Q is preferably alkylene or alkylenylene, preferably

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C<sub>2-20</sub>-alkylene, or C<sub>2-20</sub>-alkylenylene, or substituted C<sub>2-10</sub>-alkylene or substituted C<sub>2-10</sub>-alkylenylene. The organic linking groups may be interrupted by one hetero atom selected from the group of heteroatoms O and N. In a preferred embodiment the heteroatom is O or N and in a further preferred embodiment the organic aliphatic linking group Q is interrupted by one heteroatom O. When the organic aliphatic linking group Q is interrupted by N, the N may further be substituted by one substituted or unsubstituted alkyl or by one substituted or unsubstituted aryl group. The most preferred organic aliphatic linking groups Q are not interrupted by a hetero atom as for example O or N.

The substituent of Q are preferably selected from substituted or unsubstituted alkyl, hydroxy, carboxy or sulpho, preferably hydroxy-C<sub>1-4</sub>-alkyl, carboxy-C<sub>1-4</sub>-alkyl or sulpho-C<sub>1-4</sub>-alkyl; alkoxy, preferably -C<sub>1-4</sub>-alkoxy and especially methoxy; phenyl optionally substituted by C<sub>1-4</sub>-alkyl, carboxy, hydroxy, sulpho, cyano, amino or nitro, halo, preferably F or Cl; -SO<sub>3</sub>H; -COOH; -OH; -CN; or -NO<sub>2</sub>.

More preferred Q-groups are unsubstituted C<sub>1-4</sub>-alkylene groups or substituted C<sub>1-4</sub>-alkylene groups.

Examples of unsubstituted alkylene and substituted alkylene groups represented by Q include: ethylene; 1,2- and 1,3-propylene; 2-hydroxy-1,3-propylene; 1,4-, 2,3- and 2,4-butylene; 2-methyl-1,3-propylene; 2-(4'-sulphophenyl)-1,3-propylene; 2-methyl-2,4-pentylene; 2,2-dimethyl-1,3-propylene; 1-chloro-2,3-propylene; 1,6- and 1,5-hexylene; 1-(methoxycarbonyl)-1,5-pentylene; 1-carboxy-1,5-pentylene; 2,7-heptylene; and 3-methyl-1,6-hexylene.

When X or X' is a labile atom or group, it is preferably an atom or group which is displaceable by a hydroxyl group of cellulose under mildly alkaline aqueous conditions to form a covalent bond between the compound of Formula (1) and cellulose. Preferred labile atoms and groups represented by X or X' include halogens, for example F and Cl; sulphonic acid groups; thiocyno groups; quaternary ammonium. F and Cl are the most preferred labile groups.

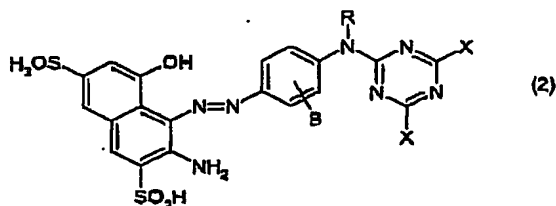
The compound of Formula (1) preferably contains only two azo groups (-N=N-).

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- The compounds of the invention may be in the free acid or salt form. Preferred salts are water-soluble. Examples of such cations are alkali metal cations, e.g. lithium, sodium, potassium, and ammonium cations or substituted ammonium cations, e.g. mono-, di-, tri- and tetra-methylammonium, tri-ethylammonium, mono-, di-, and tri-ethanolammonium, and ethoxylated mono-, di-, and tri-ethanolammonium. The preferred cations are the alkali metal cations and the ammonium cation, with the sodium cation being the most preferred.
- 10 The compounds may be converted into a salt using known techniques. For example, an alkali metal salt of a compound or the free acid may be converted into a salt with ammonia or an amine by dissolving an alkali metal salt of the compound or the free acid form respectively in water, acidifying with a mineral acid and adjusting the pH of the solution to pH 9 to 9.5 with ammonia or the amine and removing the alkali metal
- 15 cations by dialysis, reverse osmosis or ultrafiltration.

- The compounds of the invention may be prepared using conventional techniques for the preparation of azo dyes. For example a suitable method comprises condensing a compound of the Formula  $\text{HN}(\text{R}'')\text{QN}(\text{R}''')\text{H}$  with approximately 2 molar equivalents of
- 20 a compound of the Formula (2):

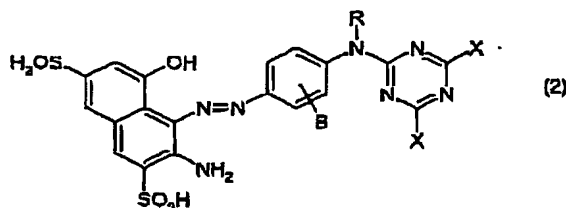


wherein Q, B, R, R'', R''' and X are as hereinbefore defined.

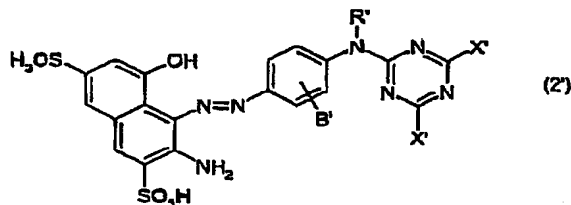
- Alternatively a further suitable method comprises condensing a compound of the
- 25 Formula  $\text{HN}(\text{R}'')\text{QN}(\text{R}''')\text{H}$  with approximately one molar equivalents of a compound of the Formula (2):

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and then reacting the reaction product of the reaction of the compound of the Formula HN(R'')QN(R''')H with the compound of the Formula (2) with a compound of Formula (2')



5

wherein B, B', Q, R, R', R'', R''', X and X' have the meaning as hereinabove defined.

The condensation is preferably performed in a liquid medium, more preferably an aqueous medium and especially water. Temperatures of 15°C to 100°C are preferred, more preferably from 30 to 40°C. Preferably a reaction time of 1 to 48, more preferably 3 to 24 hours is used.

The condensation is preferably performed in the presence of a base. The base may be any inorganic base for example, ammonia, an alkali metal or alkali earth metal hydroxide, carbonate or bicarbonate, or an organic base. Preferred organic bases are tertiary amines for example, N-alkylated heterocycles, for example N-(C<sub>1-4</sub>-alkyl)morpholine, N-(C<sub>1-4</sub>-alkyl)piperidine, N, N'-di(C<sub>1-4</sub>-alkyl)piperazine; tri(C<sub>1-4</sub>-alkyl)amines, for example triethylamine, and optionally substituted pyridines, especially pyridine. Further preferred amine compounds are mono-, di- and trimethylamine, tri-ethylamine, mono-, di-, and tri-ethanolamine, and ethoxylated mono-, di-, and tri-ethanolamine.

After the condensation the product may be isolated by precipitating the product as a salt from the reaction mixture for example by the addition of a suitable alkali metal salt, especially sodium chloride. Alternatively, the product may be isolated in its free acid form by acidifying the reaction mixture, preferably using a mineral acid, especially

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hydrochloric acid. Where the product precipitates as a solid it may be separated from the mixture by filtration.

In a new dyestuff according to the invention, the cations can be the same or different, e.g., they can also be a mixture of the above mentioned cations meaning that the dyestuff can be in a mixed salt form.

If desired unwanted anions may be removed from the product of the above process by dialysis, osmosis, ultrafiltration or a combination thereof.

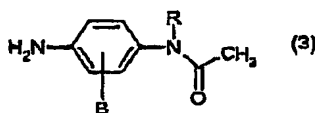
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The product of the above process may be converted, if desired, to the  $\text{NH}_4^+$ , quaternary ammonium or organic amine salt by the addition of ammonia, ammonium hydroxide, primary, secondary, tertiary or quaternary amine. When the base used in the condensation process is an organic amine an excess may be used so that the compound of formula (1) is formed as the organic amine salt.

15

The compound of the Formula (2) may be prepared using conventional techniques, for example by:

(1) diazotizing a compound of the Formula (3) to give the corresponding diazonium salt:



wherein R and B is as hereinbefore defined;

(2) coupling the diazonium salt from stage (1) with 2-amino-8-naphthol-3,6-disulphonic acid at a  $\text{pH} < 7$ , preferably at a  $\text{pH}$  of from 3 to 5;

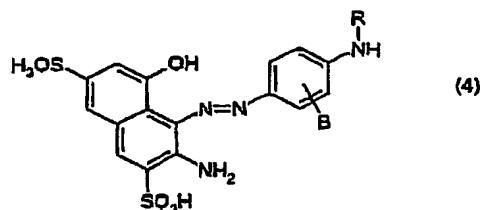
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(3) hydrolyzing the product of stage (2) under alkaline conditions to give a compound of the Formula (4):

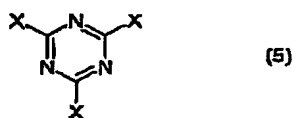


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(4) condensing the product from stage (3) with approximately 1 molar equivalent of the compound of the formula (5):



5 wherein B, R and X are as hereinbefore defined; and

The diazotization in stage (1) is preferably performed in an acidic aqueous medium in the presence of a suitable diazotization agent. Dilute mineral acid, e.g. HCl or H<sub>2</sub>SO<sub>4</sub>, is preferably used to achieve the desired acidic conditions. Conveniently the diazotization agent is formed in-situ, for example by dissolving an alkali metal nitrite, preferably sodium nitrite, in a molar excess of mineral acid, preferably HCL. Normally at least one mole of diazotization agent per mole of the compound of Formula (3), preferably from 1 to 1.25 moles will be used in the diazotization.

15 The temperature of the diazotization is not critical and may conveniently be carried out at from -5°C to 20°C, preferably from 0 to 10°C and especially from 0 to 5°C.

The hydrolysis in stage (3) is preferably performed at a pH of from 9 to 14. The temperature during hydrolysis is preferably 40 to 90°C, more preferred at 50 to 65°C.

20

When B and B', R and R' or X and X' are different, the compounds of Formula (1) are preferably prepared by condensing a compound of the Formula (2) with an approximately equimolar quantity of the compound of the formula HN(R'')QN(R''')H. The product of this reaction is then further condensed with an approximately equimolar quantity of a compound of the Formula (2) wherein R is R', B is B' and X is X' as

25 hereinbefore defined.

Alternatively, a compound of formula (1) in which one or both of X and X' are other

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than halogen, may be prepared by condensing a compound of formula (1), in which  $X = X' = \text{Cl}$  or  $\text{F}$ , with sufficient of a compound or compounds  $\text{XH}$  and/or  $\text{X'H}$ , wherein  $X$  and  $X'$  are as hereinbefore defined except for  $\text{Cl}$  or  $\text{F}$ , under such conditions of temperature and/or time as to replace one or both  $\text{Cl}$  or  $\text{F}$  atoms.

5

The compounds according to the present invention may be, and preferably are, purified to remove undesirable impurities before they are incorporated into liquid dye preparations for conventional dyeing as well as for example for inks for ink jet printing or conventional printing. Conventional techniques may be employed for purifying the dyes, for example ultrafiltration, reverse osmosis and/or dialysis. For other uses, especially for conventional (classical) printing and dyeing operations may be purified by precipitating for example by salting out as well as purified by for example ultrafiltration, reverse osmosis and/or dialysis.

15

The new dyestuff or mixtures thereof are for dyeing or printing hydroxy group- or nitrogen-containing organic substrates. Preferred substrates are leather and fiber material comprising natural or synthetic polyamides and, particularly, natural or regenerated cellulose such as cotton, viscose and spun rayon. The most preferred substrate is textile material comprising cotton.

20

Dyeing or printing is effected in accordance with known methods conventional in the dyestuff field. It is preferred to effect dyeing of fiber-reactive dyestuffs using the exhaust dyeing method at temperatures within the range of  $30 - 80^{\circ}\text{C}$ , particularly at  $50 - 60^{\circ}\text{C}$ , and with a liquor to goods ratio of 6:1 to 30:1, more preferably of 10:1.

25

The new fiber-reactive dyestuff gives good exhaust and fixation yields when used as a dyestuff. Moreover, any unfixed compound is easily washed off the substrate. The dyeings and prints derived from the new fiber-reactive dyestuff exhibit good wet fastness properties such as wash, water, sea water and sweat fastness and in particular excellent light fastness. They also exhibit good resistance to oxidation agents such as chlorinated water, hypochlorite bleach, peroxide bleach and perborate-containing washing detergents.

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The corresponding direct dyestuffs can be used as dyes directly or can be used in form of an aqueous, for example concentrated stabile solution, or in the form of their granulate in quaternary form and/or the mentioned salts of mineral acids or organic acids, for coloring fibers of all types, of cellulose, cotton or leather, particularly however paper or paper products.

The dyes can also be used in the production of pulp dyeing of bleached and unbleached paper. They can furthermore be used in dyeing paper according to the dip dyeing process.

The compounds of Formula (1) are useful as dyes, especially for the coloration of inks for ink jet printing. The dyes are also suitable for dyeing and printing in a conventional manner. The compounds exhibit a high solubility in aqueous media and provide prints and dyeings which exhibit improved high light-fastness and water-fastness when applied on a substrate or incorporated into inks for ink jet printing.

According to a second aspect of the present invention there is provided a composition comprising one or more compound(s) of the formula (I) or a salt thereof and a medium.

The compositions according to the second aspect of the invention are useful as inks, particularly printing inks and especially ink jet printing inks. The compositions according to the second aspect of the invention are useful as printing pastes, ink-jet printing inks or in a dyeing path for dyeing a substrate.

25

In addition ink jet printing is a non-impact printing technique in which droplets of ink are ejected through a fine nozzle onto a substrate without bringing the nozzle into contact with the substrate. There are many demanding performance requirements for dyes and inks used in ink jet printing. The dyes according to the invention provide sharp, non-feathered images when applied by printing techniques (classical and non-impact printing techniques) having good water-fastness, light-fastness and optical density. Details of this technology are described for example in the Ink-Jet-Printing section of R.W. Kenyon in "Chemistry and Technology of Printing and Imaging

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Systems", Peter Gregory (editor), Blackie Academic & Professional, Chapman & Hall 1996, pages 113-138, and references cited therein.

5 The medium for ink jet rinting is preferably water, a mixture of water and an organic solvent, an organic solvent free from water, or a low melting point solid. A preferred composition comprises:

- (a) from 0.01 to 30 parts of one or more compound(s) of the Formula (1) or or salt thereof as hereinbefore defined; and
- 10 (b) from 70 to 99.99 parts of a medium comprising a mixture of water and an organic solvent, an organic solvent free from water, or a low melting point solid;

wherein all parts are by weight and the number of parts of (a)+(b)=100.

15 The number of parts of component (a) is preferably from 0.1 to 20, more preferably from 0.5 to 15, and especially from 1 to 5 parts. The number of parts of component (b) is preferably from 99.9 to 80, more preferably from 99.5 to 85, especially from 99 to 95 parts.

20 When the medium is a mixture of water and an organic solvent or an organic solvent free from water, preferably component (a) is completely dissolved in component (b). Preferably component (a) has a solubility in component (b) at 20°C of at least 10%. This allows the preparation of concentrates which may be used to prepare more dilute inks and reduces the chance of the compound of Formula (1) precipitating if  
25 evaporation of the liquid medium occurs during storage.

When the medium comprises a mixture of water and an organic solvent, the weight ratio of water to organic solvent is preferably from 99:1 to 1:99, more preferably from 99:1 to 50:50 and especially from 95:5 to 80:20.

30

It is preferred that the organic solvent present in the mixture of water and organic solvent is a water-miscible organic solvent or a mixture of such solvents. Preferred water-miscible organic solvents include C<sub>1-4</sub>-alkanols, preferably methanol, ethanol,

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n-propanol, isopropanol, n-butanol, sec-butanol, tert-butanol, n-pentanol, cyclopentanol and cyclohexanol; linear amides, preferably dimethylformamide or dimethylacetamide; ketones and ketone-alcohols, preferably acetone, methyl ether ketone, cyclohexanone and diacetone alcohol; water-miscible ethers, preferably tetrahydrofuran and dioxane; 5 diols, preferably diols having from 2 to 12 carbon atoms, for example pentane-1,5-diol, ethylene glycol, propylene glycol, butylene glycol, pentylene glycol, hexylene glycol and thiodiglycol and oligo- and poly-alkyleneglycols, preferably diethylene glycol, triethylene glycol, polyethylene glycol and polypropylene glycol; triols, preferably glycerol and 1,2,6-hexanetriol; mono-C<sub>1-4</sub>-alkyl ethers of diols, preferably 10 mono-C<sub>1-4</sub>-alkyl ethers of diols having 2 to 12 carbon atoms, especially 2-methoxyethanol, 2-(2-methoxyethoxy)ethanol, 2-(2-ethoxyethoxy)-ethanol, 2-(2-(2-methoxyethoxy)ethoxy)ethanol, 2-[2-(2-ethoxyethoxy)-ethoxy]-ethanol and ethyleneglycol monoallylether, cyclic amides, preferably 2-pyrrolidone, N-methyl-2-pyrrolidone, N-ethyl-2-pyrrolidone, caprolactam and 1,3-dimethylimidazolidone; cyclic 15 esters, preferably caprolactone; sulfoxides, preferably dimethyl sulfoxide and sulfolane. Preferably the liquid medium comprises water and 2 or more, especially from 2 to 8, water-soluble organic solvents.

Especially preferred water-soluble organic solvents are cyclic amides, especially 2- 20 pyrrolidone, N-methyl-pyrrolidone and N-ethyl-pyrrolidone; diols, especially 1,5-pentane diol, ethyleneglycol, thiodiglycol, diethyleneglycol and triethyleneglycol; and mono- C<sub>1-4</sub>-alkyl and C<sub>1-4</sub>--alkyl ethers of diols, more preferably mono- C<sub>1-4</sub>-alkyl ethers of diols having 2 to 12 carbon atoms, especially 2-methoxy-2-ethoxy-2-ethoxyethanol.

25 A preferred medium comprises:

- (a) from 75 to 95 parts water; and
  - (b) from 25 to 5 parts in total of one or more solvents selected from diethylene glycol, 2-pyrrolidone, thiodiglycol, N-methylpyrrolidone, cyclohexanol, caprolactone, caprolactam and pentane-1,5-diol;
- 30 wherein the parts are by weight and the sum of the parts (a) and (b) = 100.

Examples of further suitable media comprising a mixture of water and one or more organic solvents are described in US 4,963,189, US 4,703,113, US 4,626,284 and EP

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4,251,50A.

When the liquid medium comprises an organic solvent free from water, (i.e. less than 1% water by weight) the solvent preferably has a boiling point of from 300 to 200°C, more preferably of from 40°C to 150°C, especially from 50°C to 125°C. The organic solvent may be water-immiscible, water-miscible or a mixture of such solvents. Preferred water-miscible organic solvents are any of the hereinbefore described water-miscible organic solvents and mixtures thereof. Preferred water-immiscible solvents include, for example, aliphatic hydrocarbons; esters, preferably ethyl acetate; chlorinated hydrocarbons, preferably  $\text{CH}_2\text{Cl}_2$  and ethers, preferably diethyl ether; and mixtures thereof.

When the liquid medium comprises a water-immiscible organic solvent, preferably a polar solvent is included because this enhances solubility of the dye in the liquid medium. Examples of polar solvents include  $\text{C}_{1-4}$ -alcohols. In view of the foregoing preferences it is especially preferred that where the liquid medium is an organic solvent free from water it comprises a ketone (especially methyl ethyl ketone) or an alcohol (especially a  $\text{C}_{1-4}$ -alkanol, more especially ethanol or propanol).

The organic solvent free from water may be a single organic solvent or a mixture of two or more organic solvents. It is preferred that when the medium is an organic solvent free from water it is a mixture of 2 to 5 different organic solvents. This allows a medium to be selected which gives good control over the drying characteristics and storage stability of the composition.

25

Media comprising an organic solvent free from water are particularly useful where fast drying times are required and particularly when printing onto hydrophobic and non-absorbent substrates, for example plastics, metal and glass.

Preferred low melting solid media have a melting point in the range from 60°C to 125°C. Suitable low melting point solids include long chain fatty acids or alcohols, preferably those with  $\text{C}_{1-24}$  chains, and sulphonamides. The compound of Formula (1) may be dissolved in the low melting point solid or may be finely dispersed in it.

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The compounds according to the present invention exhibit a high solubility in aqueous media, accordingly it is preferred that the liquid medium is water or more preferably a mixture of water and one or more water miscible organic solvent(s).

5

The composition may also contain additional components conventionally used in ink jet printing inks, for example viscosity and surface tension modifiers, corrosion inhibitors, biocides, kogation reducing additives and surfactants which may be ionic or non-ionic.

- 10 When a composition according to the second aspect of the present invention is used as an ink jet printing ink, the ink preferably has a concentration of less than 100 parts per million, more preferably less than 50 parts per million, in total of halide ions and divalent and trivalent metals. This reduces nozzle blockage in ink jet printing heads, particularly in thermal ink jet printers.

15

A third aspect of the present invention provides a process for printing an image on a substrate comprising applying thereto an ink containing a compound of Formula (1) by means of an ink jet printer.

- 20 The ink used in this process preferably comprises a composition as defined in the second aspect of the present invention.

- The ink jet printer preferably applies the ink to the substrate in the form of droplets which are ejected through a small orifice onto the substrate. Preferred ink jet printers are
- 25 piezoelectric ink jet printers and thermal ink jet printers. In thermal ink jet printers, programmed pulses of heat are applied to the ink in a reservoir by means of a resistor adjacent to the orifice, thereby causing the ink to be ejected in the form of small droplets directed towards the substrate during relative movement between the substrate and the orifice. In piezoelectric ink jet printers the oscillation of a small crystal causes
- 30 ejection of the ink from the orifice.

The substrate is preferably paper, plastic, a textile, metal or glass, more preferably paper, an overhead projector slide or a textile material, especially a textile material.

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When the substrate is a textile material the ink according to the invention is preferably applied thereto by:

- i) applying the composition to the textile material using an ink jet printer, and
- 5 ii) heating the printed textile material at a temperature of from 50°C to 250°C.

Preferred textile materials are natural, synthetic and semi-synthetic materials. Examples of preferred natural textile materials include wool, silk, hair and cellulosic materials, particularly cotton, jute, hemp, flax and linen. Examples of preferred synthetic and  
10 semi-synthetic materials include polyamides, polyesters, polyacrylonitriles and polyurethanes.

Preferably the textile material has been treated with an aqueous pre-treatment composition comprising a thickening agent and optionally a water-soluble base and a  
15 hydrotropic agent and dried prior to step i) above.

The pre-treatment composition preferably comprises a solution of the base and the hydrotropic agent in water containing the thickening agent. Particularly preferred pre-treatment compositions are described more fully in EP534660A1.

20

According to a fifth aspect of the present invention there is provided an ink jet printer cartridge containing an ink, characterized in that the ink contains one or more compound(s) of the Formula (1) or salts thereof as defined in the first aspect of the invention.

25

Preferably the ink contained in the ink jet printer cartridge is an ink according to the second aspect of the present invention.

30

The invention is further illustrated by the following Examples in which all parts and percentages are by weight unless otherwise stated.



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**Example 1**

Dye (1) was prepared using the process described below:

**Stage (i) : Diazotization and Coupling**

To N-acetyl-p-phenylenediamine sulphonic acid (0.5 moles) in water (800ml) was  
5 added concentrated hydrochloric acid (150ml) and the solution was cooled to 0-5°C. 2N  
sodium nitrite (250ml) was added dropwise over 60 minutes with stirring. After 15  
minutes, excess nitrous acid was destroyed by the addition of sulphaminic acid (0.2g).  
To the resulting suspension was added a solution of 2-amino-8-naphthol-3,6-  
disulphonic acid (0.5 moles in 700ml of water at pH = 6) and the pH was adjusted to 4  
10 by the addition of sodium acetate. The mixture was stirred at 0-5°C for 4 hours before  
being allowed to warm to room temperature.

**Stage (ii) Hydrolysis**

The acetyl group present on the product of stage (i) was removed by alkaline hydrolysis  
15 by adding concentrated sodium hydroxide (200ml) to the mixture resulting from stage I  
and heating at 60-65°C for 15 hours.

After cooling to room temperature, the pH was adjusted to 7 by the addition of  
concentrated hydrochloric acid. Sodium chloride (20% weight-volume) was added and  
20 the precipitated solid was collected by suction filtration, washed with 30% brine and  
dried at 70°C. Yield 210g (strength 50%).

**Stage (iii) Condensation with Cyanuric Chloride**

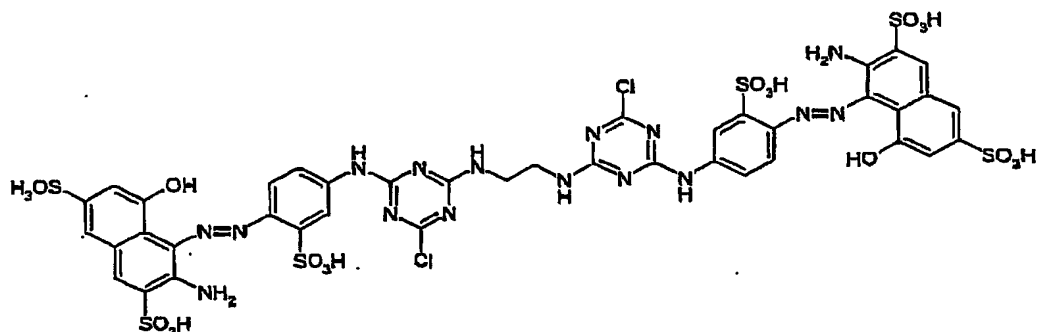
The product from stage (ii) (208g) was dissolved in water (1600ml) at pH 7 and cooled  
25 to 5-10°C. Cyanuric chloride (37g) in acetone (200ml) was added dropwise with stirring  
over a period of 30 minutes and the mixture was stirred for a further 1 hour. The pH of  
the solution was kept at a value of 4 to 5 by addition of sodium carbonate.

**Stage (iv) Condensations**

30 Ethylenediamine (6.2 g) was added and the mixture was stirred at 30°C for 7 hours. The  
pH of the solution was kept at a value of 7 to 8 by addition of sodium carbonate. The  
precipitated dyestuff was filtered off and was dried at 70°C under reduced pressure.  
Yield 200 g (strength 64 %).  $\lambda(\text{max})$  was 524 nm.

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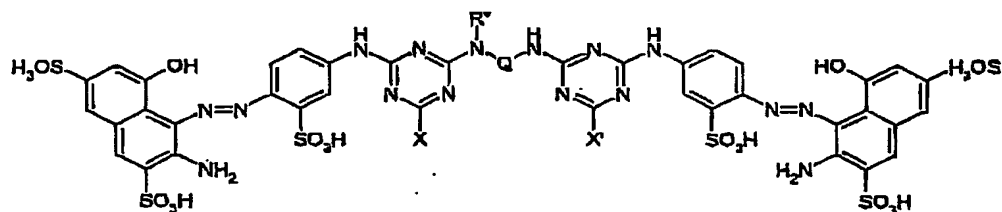
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Its dyeing on cotton shows a bluish-red shade with outstanding lightfastness properties.

### Examples 2 to 8

#### 5 Dyes of the formula:



were prepared by condensing the compound  $\text{HR}''\text{N-Q-NH}_2$  shown in Table 1 with approximately 2 molar equivalents of the product of stage (iii) in Example 1. The reaction conditions used were analogous to those used in stage (iv) of Example 1. For the derivatives wherein X and/or X' signifies F the corresponding cyanuric fluoride was reacted without acetone and the reaction was carried out at  $-5^\circ\text{C}$  in the Stage (iii) Condensation with cyanuric fluoride.

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Table 1

Example	H <sub>2</sub> N-Q-NHR''	X and X'	λ (max)
2	H <sub>2</sub> N-CH <sub>2</sub> -CH <sub>2</sub> -CH <sub>2</sub> -NH <sub>2</sub>	Cl	521
3	H <sub>2</sub> N-CH <sub>2</sub> -CH(OH)-CH <sub>2</sub> -NH <sub>2</sub>	Cl	520
4	H <sub>2</sub> N-CH <sub>2</sub> -CH(CH <sub>3</sub> )-NH <sub>2</sub>	Cl	524
5	H <sub>2</sub> N-CH <sub>2</sub> -CH <sub>2</sub> -NH-CH <sub>3</sub>	Cl	520
6	H <sub>2</sub> N-CH <sub>2</sub> -CH <sub>2</sub> -NH <sub>2</sub>	F	522
7	H <sub>2</sub> N-CH <sub>2</sub> -CH(OH)-CH <sub>2</sub> -NH <sub>2</sub>	F	519
8	H <sub>2</sub> N-CH <sub>2</sub> -CH(CH <sub>3</sub> )-NH <sub>2</sub>	F	523
9	H <sub>2</sub> N-CH <sub>2</sub> -CH <sub>2</sub> -CH <sub>2</sub> -NH <sub>2</sub>	F	520
10	H <sub>2</sub> N-CH <sub>2</sub> -CH <sub>2</sub> -NH-CH <sub>3</sub>	F	520

5

The following examples illustrate the possibilities of use of the described dyestuffs. The chlorine-containing dyestuffs are dyed according to Application Example A and the fluorine-containing dyestuffs according to Application Example B.

#### 10 Application Example A

A dye bath consisting of 1000 parts of demineralized water, 80 parts of Glauber's salt (calcined), 1 part of sodium salt of 1-nitrobenzene-3-sulphonic acid and 1 part of the dyestuff from Example 1 was heated to 80 °C over the course of 10 minutes. Thereafter, 100 parts of mercerized cotton were immersed in the resultant solution. Dyeing was effected at 80 °C over 5 minutes before the solution was raised to 95 °C over 15 minutes. After 10 minutes at 95 °C, 3 parts of soda were added, followed by a further 7 parts of soda after 20 minutes, and another 10 parts of soda after 30 minutes at 95 °C. Dyeing subsequently continued for 60 minutes at 95 °C. The dyed material was then removed from the dye bath, and rinsed for 2 minutes under running demineralized water at 60 °C ± 10 °C and for 1 minute under running tap water at 60 °C ± 10 °C. The material was then washed twice for 10 minutes, each time in 5000 parts of boiling demineralized water, and subsequently rinsed for 2 minutes under running

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demineralized water at  $60\text{ }^{\circ}\text{C} \pm 10\text{ }^{\circ}\text{C}$ , 1 minute under running tap water at  $60\text{ }^{\circ}\text{C} \pm 10\text{ }^{\circ}\text{C}$  and 1 minute under cold tap water. After drying, a bluish-red cotton dyeing with good fastness was obtained.

#### 5 Application Example B

To the dyebath containing in 100 parts of demineralized water 5 parts of Glauber's salt (calcined), 10 parts of cotton fabric (bleached) are added. The bath is heated to  $50\text{ }^{\circ}\text{C}$  within 10 minutes, and 0.5 part of the dyestuff of Example 6 is added. After 25 minutes  
10 at  $50\text{ }^{\circ}\text{C}$ , 0.7 parts of soda were added, followed by a further 1.3 parts of soda after 20 minutes, and another 2 parts of soda after 30 minutes at  $50\text{ }^{\circ}\text{C}$ . The bath was subsequently heated over the course of 15 minutes to  $60\text{ }^{\circ}\text{C}$ ., and dyeing continued for 60 minutes at  $60\text{ }^{\circ}\text{C}$ . The dyed material was then removed from the dye bath, and rinsed for 2 minutes under running demineralized water at  $60\text{ }^{\circ}\text{C} \pm 10\text{ }^{\circ}\text{C}$ . and for 1 minute  
15 under running tap water at  $60\text{ }^{\circ}\text{C} \pm 10\text{ }^{\circ}\text{C}$ . The dyed material was then washed twice for 10 minutes, each time in 5000 parts of boiling demineralized water, and subsequently rinsed for 2 minutes under running demineralized water at  $60\text{ }^{\circ}\text{C} \pm 10\text{ }^{\circ}\text{C}$  , 1 minute under running tap water at  $60\text{ }^{\circ}\text{C} \pm 10\text{ }^{\circ}\text{C}$  and 1 minute under cold tap water. After drying, a bluish-red cotton dyeing with good fastness was obtained.

20

The dyestuffs of Examples 2 to 8 or dyestuff mixtures of Examples 1 to 8 were used for dyeing cotton in an analogous manner to that described in Examples A and B. bluish-red dyeings were obtained, which displayed good fastness properties.

#### 25 Application Example C

A printing paste having the components

- 40 parts of the dyestuff of Example 1
- 30 100 parts of urea
- 330 parts of water
- 500 parts of a 4% sodium alginate thickener
- 10 parts of the sodium salt of 1-nitrobenzene-3-sulphonic acid

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20 parts of soda

1000 parts in all

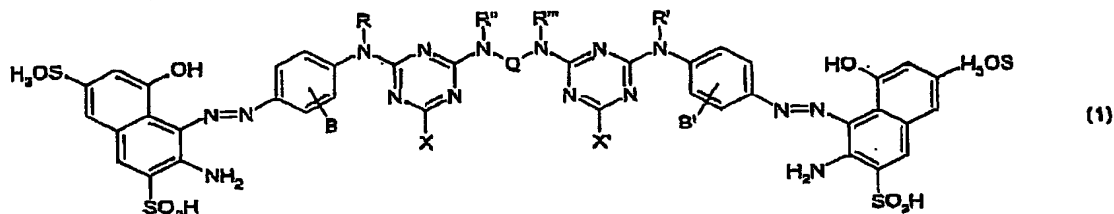
- was applied to cotton material by conventional printing processes. The printed and dried
- 5 material was steamed for 4-8 minutes at 102°C to 105 °C. before being given a cold and a hot rinse. The fixed cotton material was subsequently washed at the boil (analogously to Example A) and dried. The bluish-red print obtained had good all-round fastness properties.
- 10 The dyestuffs of examples 2 to 8 were also used for printing cotton analogously to the method of example C. In all cases, bluish-red prints with good fastness properties were obtained.

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## CLAIMS

1. A compound of Formula (1) and salts thereof:



wherein:

- B and B' are each independently -SO<sub>3</sub>H, -COOH, substituted alkoxy, substituted alkyl, unsubstituted alkoxy, unsubstituted alkyl, or -PO<sub>3</sub>H<sub>2</sub>;
- Q is an organic aliphatic linking group;
- R, R', R'' and R''' are each independently H or unsubstituted or substituted alkyl;
- X and X' are each independently a labile atom or group ;

2. A compound according to claim 1 characterized in that the organic aliphatic linking group Q is alkylene, preferably C<sub>2-20</sub>-alkylene, or C<sub>2-20</sub>-alkylenylene.

3. A compound according to claim 2 characterized in that the organic aliphatic linking group Q is C<sub>1-4</sub>-alkylene groups or substituted C<sub>1-4</sub>-alkylene groups.

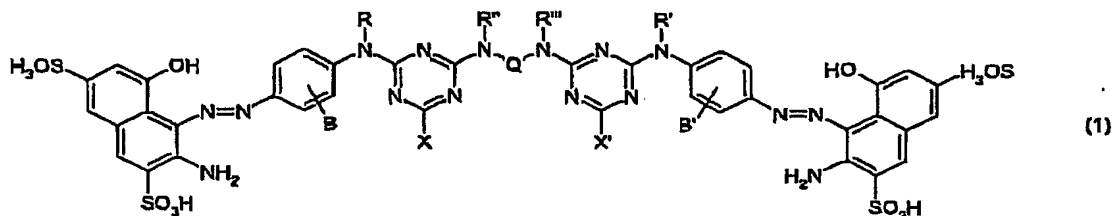
4. A compound according to any claim 1 to 3 characterized in that X or X' both are F or Cl.

5. A compound according to any claim 1 to 4 characterized in that B or B' both are ortho to the diazo bridge and signify -SO<sub>3</sub>H.

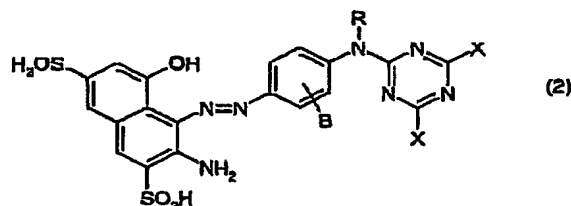
6. A process for the production of the compounds of formula (1)

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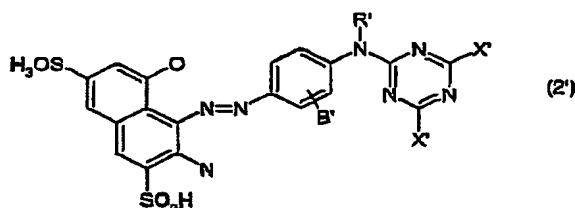
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which comprising the steps of  
comprises condensing a compound of the Formula  $\text{HN(R'')QN(R''')H}$  with  
approximately one molar equivalents of a compound of the Formula (2):



and then reacting the reaction product of the compound of the Formula  
 $\text{HN(R'')QN(R''')H}$  with the compound of the Formula (2) with a compound of Formula  
(2')



wherein B, B', Q, R, R', R'', R''', X and X' have the meaning as hereinabove defined.

7. A process of dyeing or printing or ink jet printing hydroxy-group-containing or nitrogen containing organic substrates, wherein the dyeing or printing is effected with compounds according to any one of the claims 1 to 4, their salts or with mixtures thereof.

8. A process according to claim 7, for dyeing or printing leather or fibrous materials, which consist of or contain natural or synthetic polyamides or natural or regenerated cellulose.

20

9. Process according to either of the claims 7 or 8, for dyeing or printing or ink jet printing textile material, which consists of or contains cotton.

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10. Hydroxy group-containing or nitrogen containing substrates which are dyed or printed or ink jet printed in accordance with any of the claims 7 to 9.

5 11. The use of compounds according to any one of the claims 1 to 4, their salts or mixtures thereof in dyeing or printing or ink jet printing hydroxy group-containing or nitrogen containing substrates.

10 12. Ink jet inks comprising compounds according to any one of the claims 1 to 4, their salts or mixtures thereof

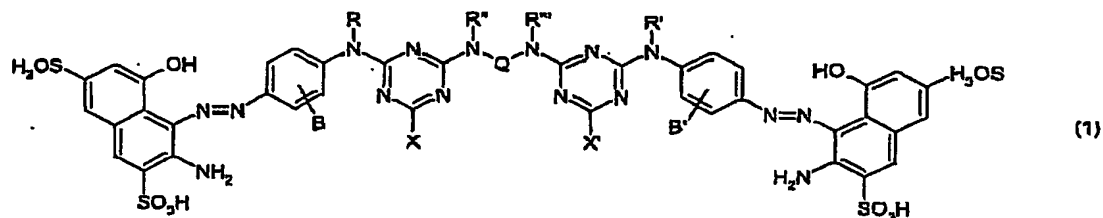


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**ABSTRACT**

A dyestuff according to formula (1)



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or a salt thereof wherein the substituents have the definitions as defined in claim 1.

The dyestuffs are useful for dyeing or printing nitrogen-containing or hydroxy-group-containing organic substrates and for the production of (ink-jet) printing inks.

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